Influence of Monomer Optical Purity on the Conformation and Properties of Chiral, Donor-Embedded Polybinaphthalenes for Nonlinear Optical Purposes

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A series of chiral, chromophore-functionalized donor-embedded polybinaphthalenes were prepared by a Stille coupling reaction between a diiodo-functionalized chromophore and a bis(trimethyltin)binaphthalene derivative. The optical purity of the chiral binaphthalene monomer was varied, and its influence on the conformation of the polymers was investigated. Differential scanning calorimetry and second-harmonic generation experiments revealed that the mobility of the chromophore in the polymers, prepared from optically impure monomers, is much higher than that in polymers obtained by polymerization of optically pure monomers. Hyper-Rayleigh scattering measurements demonstrated that this difference in mobility is due to a different macromolecular structure.

Introduction

Chiral, helical polymers have been shown to be of great interest in several fields, including photonics, electronics, and nonlinear optics (NLOs). Several interesting NLO phenomena in chiral media have been theoretically predicted,[1] and some of them have been verified experimentally in chiral, helical polymeric media.[2] Also chiral, helical, chromophore-functionalized polybinaphthalenes have already been prepared[3]. In such donor-embedded polymers, the chiral ordering of the chromophores remains present, even after corona poling (to induce the necessary polar ordering), and chiral contributions to the NLO response are present.[3b,f]

A helix is a highly regular structure in which all bonds that form the helix have the same configuration (either *S* or *R*). Therefore, if both *S* and *R* enantiomers are randomly incorporated into one polymer strand, not a helical, but a random-coil-like structure is obtained. As a consequence, there are two possibilities when an optically impure sample (enantiomeric excess (ee) $<100\%$) of chiral monomers is polymerized: either both enantiomers are randomly incorporated, resulting in a random-coil-like structure, or the enantiomers preferably react with monomers of the same configuration (i.e., *S* with *S* and *R* with *R*), and a structure, which is most likely helical, is obtained. The ratio of *R* and *S* monomers in the feed is then reflected in the ratio of M (right-handed) and P (left-handed) helices, respectively. In this study, we show that polymerizing an optically impure mixture of binaphthalene monomers leads to nonhelical polymers, and the differences in NLO properties between polymers, prepared from optically pure and impure monomers, are discussed.

Pu et al. already indicated that there is no preference for binaphthalene monomers of the same (or opposite) configuration in the particular case when chiral binaphthalenediboronic acids are reacted with an excess of racemic dibromobinaphthalene monomers.[4] However, no evidence was presented that there is a difference in *conformation* of these (oligomeric) materials and samples of helical polymers. Here, we show that, starting from an optically impure (containing both *R* and *S* monomers) feed, no helical polymers are obtained. Hyper-Rayleigh scattering and coher-

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Table 1. Properties of the Polymers and Blends

polymer	x_S/y_R feed	$x_{S'}/y_{R'}$,[a] polymer	yield/ %	$\bar{M}_w$[b]/ kg/mol	T_g/ °C
pol(S_{100})	100/0	100/0	98	8.0	186
pol($S_{95}R_5$)	95/5	95/5	82	3.9	165
pol($S_{90}R_{10}$)	90/10	90/10	94	3.4	168
pol($S_{80}R_{20}$)	80/20	80/20	81	4.4	167
pol($S_{50}R_{50}$)	50/50	50/50	86	3.5	164
pol(R_{100})	0/100	0/100	79	6.6	185

blend	pol(S_{100})/ pol(R_{100})	T_g/ °C	blend	pol(S_{100})/ pol(R_{100})	T_g/ °C
blend($P_{95}M_5$)	95/5	188	blend($P_{80}M_{20}$)	80/20	187
blend($P_{90}M_{10}$)	90/10	184	blend($P_{50}M_{50}$)	50/50	184

[a] Determined by CD spectroscopy. [b] Measured by GPC toward polystyrene.

ent second-harmonic generation were used to study the macromolecular conformation of the polymers.

Experimental Section

Reagents. All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, and Avocado. Reagent grade solvents were dried when necessary and purified by distillation.

The glass transition temperatures were measured with a DSC-7 apparatus from Perkin-Elmer at a heating rate of 50 °C/min (polymers) or 30 °C/min (chromophores). Gel permeation chromatography (GPC) measurements were done with a Waters apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz spectrometer.

Polymer Synthesis. A typical procedure is as follows: A solution of 156 mg (200 μmol) of **1**, 138 mg (200 μmol) of **2**, 4.58 mg (5.0 μmol) of Pd_2dba_3, and 12.3 mg (40.0 μmol) of $AsPh_3$ in 10 mL of dry THF was purged with argon and then refluxed for 64 h. After cooling, the polymer was precipitated in methanol and filtered. For purification, the polymer was redissolved in THF, precipitated in methanol, and filtered. This procedure was repeated twice.

Results and Discussion

Synthesis and Properties of the Polymers. The polymers were obtained by a Stille polycondensation reaction of a diiodo-substituted chromophore, **2**,[3h] and a bis(trimethyltin)-binaphthalene derivative, (*S*)-**1**[3b] or (*R*)-**1** or a combination thereof (Figure 1).

All polymers are soluble in common organic solvents, e.g., dichloromethane, chloroform, and tetrahydrofuran (THF). ^{1}H NMR spectroscopy confirms the proposed structure, without any visual defects.

The composition and physical properties of the polymers are listed in Table 1. For convenience, we used the following abbreviation for the polymers: pol($S_{x'}R_{y'}$), where x' and y' refer to the concentrations (mol %) of (*S*)- and (*R*)-binaphthalene enantiomers, respectively, in the polymer. For comparison, we have also included physical data on a series of blends composed of pol(S_{100}) and pol(R_{100}) polymers (abbreviated as blend(P_xM_y) with x as the concentration (mol %) of pol(S_{100}) and y the concentration (mol %) of pol(R_{100}) in the blend).

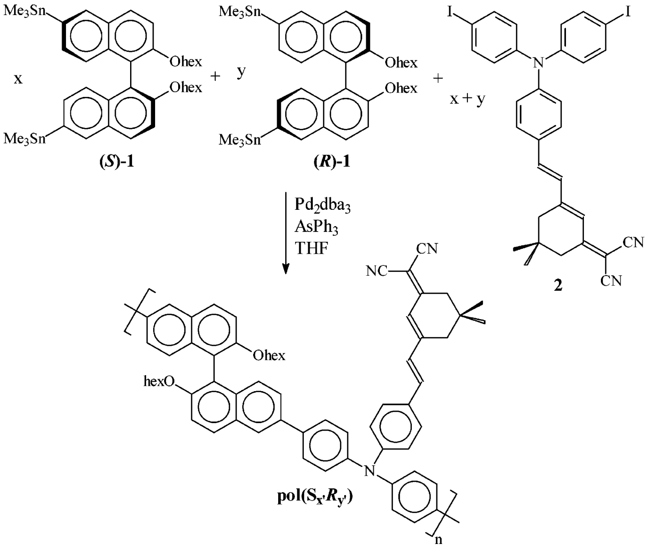

Figure 1. Synthesis and structure of the polymers.

Since there is no extended conjugation between the naphthalene units in binaphthalene, circular dichroism (CD) spectroscopy gives no information on the macromolecular structure, and it cannot be used to detect possible differences in its structure. However, it is a tool to measure the ratio of (*R*)- and (*S*)-binaphthalene enantiomers present in the polymer. We have used the ellipticity at 273 nm in THF solution to determine this ratio for the polymers, prepared from optically impure monomers. The ratio of the feed (x_S/y_R) corresponds very well with the ratio in the polymers ($x_{S'}/y_{R'}$). This is consistent with the high yields. CD spectra of thin films are essentially the same as those of the polymer solutions.

The molar masses were determined by GPC and matrix-assisted laser desorption ionization time-of-flight spectroscopy (MALDI-TOF).[3h] These results indicate that optimized reaction conditions, together with the use of diiodo instead of dibromo compounds, resulted in polymers with significantly higher molar masses. The absolute number-average molar mass ($\bar{M}_n$) of pol(S_{100}) was determined by MALDI-TOF as 5.0 kg/mol, which corresponds to eight repeating units. Moreover, in contrast with the GPC results, the molar masses of all polymers are more or less the same.

The glass transition temperature (T_g) of the polymers as well as of the blends was measured with differential scanning calorimetry (DSC) at a heating rate of 50 °C/min. It has previously been shown[3c,d,h] that the observed T_g of chromophore-functionalized polybinaphthalenes is the T_g of the chromophores in the polymer matrix and not of the whole

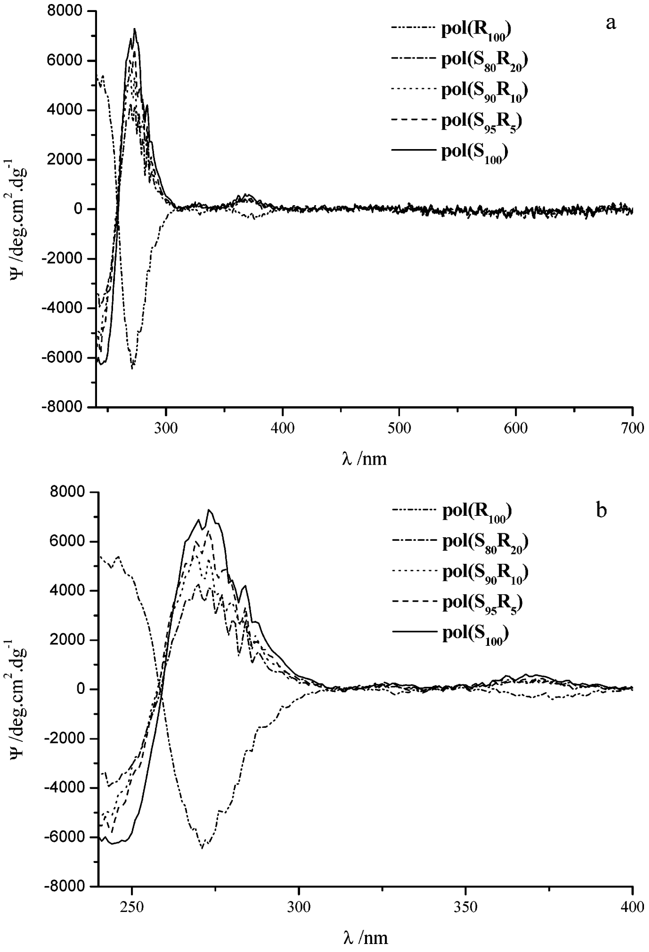

Figure 2. CD spectra of the polymers in THF solution: (a) 240−700 nm (b) 240−400 nm.

material. Therefore, the T_g of those polymers depends on the T_g of the chromophore incorporated and of the mobility of the chromophore in the material. Since the chromophore is the same in all samples, determination of the T_g is a first tool to probe possible differences in macromolecular structure. The T_g of the polymers prepared from enantiomerically pure monomers and blends thereof differs significantly from that of the polymers prepared from an enantiomerically impure feed (Table 1). Hence, this clearly points to a different conformation in both types of polymers.

SHG Properties. In a second series of experiments, thin films of the polymer materials were prepared by spin-coating a chloroform solution onto ITO glass slides. Macroscopic polar order was created by corona poling for 20 min at 7 °C above the observed T_g. The NLO properties of the films were measured by coherent second-harmonic generation (SHG) at 1064 nm. In the absence of dipolar interactions between the chromophores, the (macroscopic) second-order susceptibility $\chi^{(2)}$ of poled samples depends on the hyperpolarizability β of the chromophores incorporated and the poling efficiency.[5] As presented in Figure 3, $\chi^{(2)}$ of the helical polymers pol(S_{100}) and pol(R_{100}) is significantly lower than $\chi^{(2)}$ of the polymers obtained from optically impure binaphthalene monomers. Hence, since the chromophore and poling conditions were the same in all samples, we must conclude

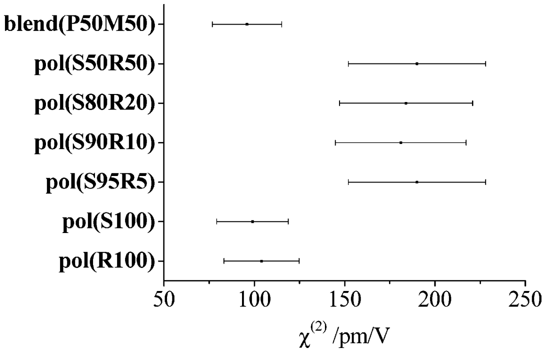

Figure 3. SHG response of polymers and blend($P_{50}M_{50}$).

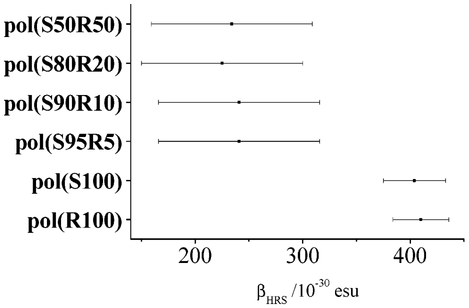

Figure 4. HRS of the polymers.

that the mobility of the chromophores in the polymers, obtained from optically impure samples, is different (higher) from that in the analogous helical polymers and blends thereof, which is consistent with the T_g results obtained form DSC. Again, these data suggest a difference in macromolecular structure.

Hyper-Rayleigh Scattering Studies. Finally, we have also carried out hyper-Rayleigh scattering (HRS) measurements on the polymers. HRS is a nonlinear scattering technique (noncoherent second-harmonic generation) to measure the hyperpolarizability of molecules and polymers in solution. The technique is very useful for the study of macromolecules since it is extremely sensitive to the macromolecular configuration.[6] The HRS response of a macromolecular ensemble of dipolar scatterers (charge-transfer chromophores) is determined by the vectorial addition of the individual hyperpolarizability of the (dipolar) chromophore along the polymer backbone. In the limit of all chromophores oriented parallel to the polymer backbone, the HRS response will be enhanced (with respect to a polymer where all chromophores are randomly oriented) by a factor of *n*, where *n* is the number of chromophores in the polymer. In general, the average angle between the chromophores and the backbone is the crucial parameter. A large angle leads to a large degree of vector cancellation; a small angle results in a large response. Hence, one could expect a significantly larger HRS response for a helical polymer vs a random-coil polymer.

As shown in Figure 4, the HRS response of the polymers prepared from the optically impure monomers is significantly

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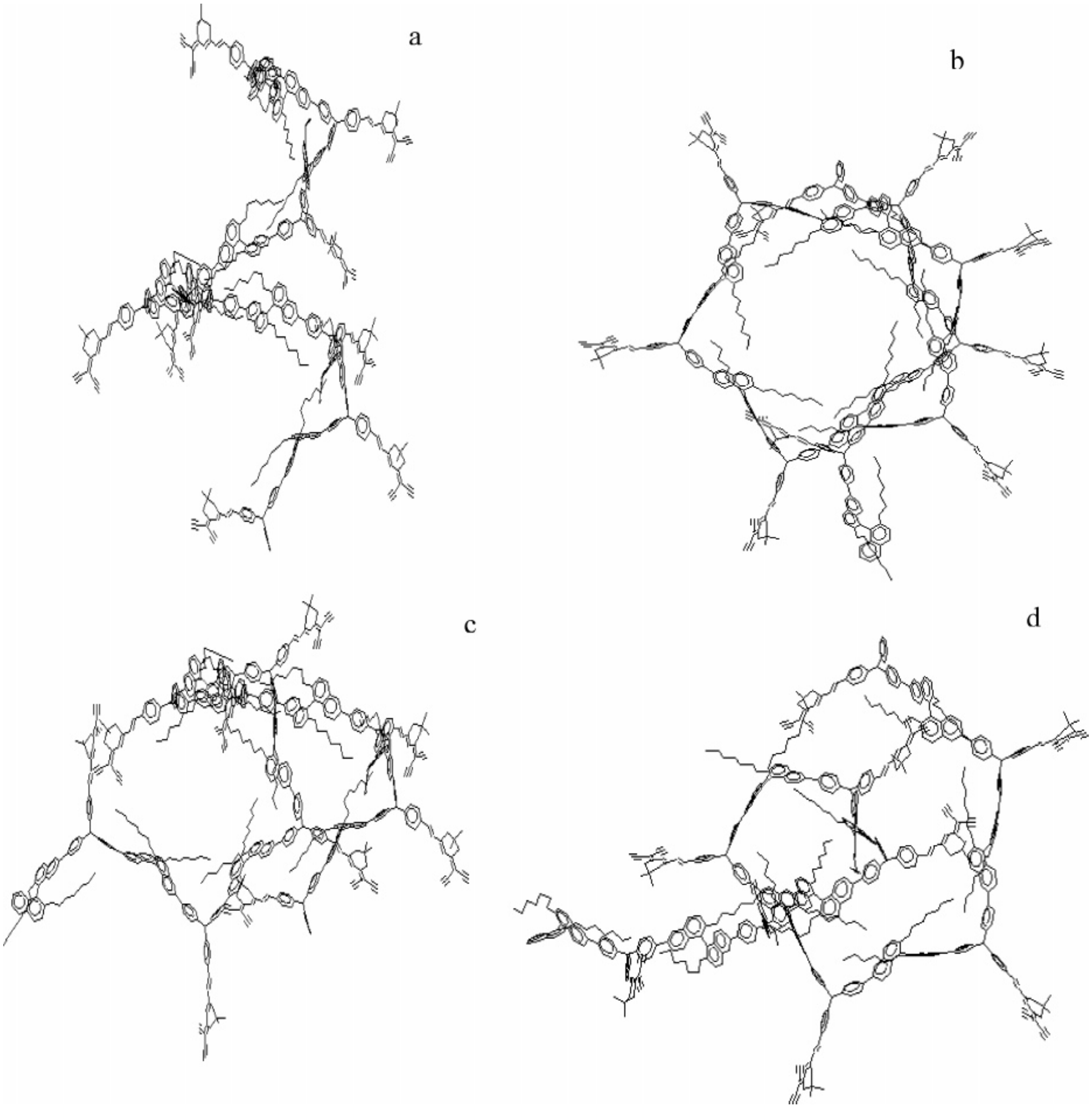

Figure 5. Molecular mechanics simulations: (a) front view and (b) top view of pol(S_{100}), (c) front view and (d) top view of pol(S_{100}) in which one (R)-binaphthalene moiety is incorporated.

smaller than the response of the polymers from optically pure monomers. This clearly points to the different macromolecular orientations in these two classes of polymers: a large average angle between the chromophores in the former and a small average angle in the latter. This is consistent with the random-coil-like structure for pol($S_{50}R_{50}$)−pol($S_{95}R_5$) and with the helical structure for pol(S_{100}) and pol(S_{100}).

To visualize the helical structure of polymers obtained from optically pure binaphthalene monomers, we performed a molecular mechanics simulation modeling of pol(S_{100}) (Hyperchem 7.1). Eight repeating units were used. As can be seen in Figure 5a,b, the polymer adopts a helical conformation. On the other hand, if the configuration of a central binaphthalene moiety is reversed (S becomes R), the helical conformation of the polymer is destroyed and a random-coil-like structure is obtained (Figure 5c,d).

Conclusions

We have demonstrated that polymerization from optically impure binaphthalene monomers leads to nonhelical polymers. DSC and SHG measurements indicated a higher mobility of the chromophores in the random-coil-like polymers, compared to the helical polymers. HRS experiments directly demonstrated a difference in macromolecular structure. Moreover, these results confirm that there is no preference for enantiomers to react with monomers of the same configuration.

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